

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE July, 2000		3. REPORT TYPE AND DATES COVERED Final 3/15/95- 1/14/99
4. TITLE AND SUBTITLE Study of Multicomponent Diffusion in Polymers Using FTIR-ATR Spectroscopy			5. FUNDING NUMBERS DAAH04-95-1-0133	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Johns Hopkins University 3400 N. Charles St. Baltimore, MD 21218			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 33870.4-CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The specific aim of this project was to study the diffusion of complex mixtures, some of which are capable of self-association and solvation, in polymers. The focus was primarily on rubbery polymers, but a glassy polymer was also studied. Diffusion coefficients were measured with FTIR-ATR spectroscopy, a powerful technique that can monitor individual components in a mixture and can also detect association or solvation interactions through changes in the infrared spectrum. Transport equations that incorporate these interactions were developed and tested. The following systems were studied: (1) the diffusion of pure methyl ethyl ketone (MEK) and MEK/toluene mixtures at various vapor phase activities in polyisobutylene (PIB), (2) the diffusion of acrylonitrile from the liquid phase in conformational isomers of a polyurethane, (3) the diffusion of methanol in glassy polycarbonate, and (4) the diffusion of methanol and ethanol in polybutadiene as a function of temperature. In addition to the experimental measurements, mathematical models were developed to determine the effect of association and solvation on the transport of small molecules in polymeric sorbents and barrier materials.				
14. SUBJECT TERMS Diffusion, Permeation, Barrier, Mixtures, Polymers, Spectroscopy			15. NUMBER OF PAGES 4 not incl. cover	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Study of Multicomponent Diffusion in Polymers Using FTIR-ATR Spectroscopy

Final Progress Report
15 March 1995 - 14 January 1999

List of Manuscripts

Published:

T. A. Barbari, S. S. Kasargod, and G. T. Fieldson, "Effect of Unequal Transport Rates and Intersolute Solvation on the Selective Batch Extraction of a Dilute Mixture with a Dense Polymeric Sorbent", *Ind. Eng. Chem. Res.*, 35, 1188-1194 (1996).

S. S. Kasargod and T. A. Barbari, "Permeation Breakthrough Models for Associating and Solvating Penetrants in a Membrane," *Ind. Eng. Chem. Res.*, 36, 483-492 (1997).

S. U. Hong, T. A. Barbari, and J. M. Sloan, "Diffusion of Methyl Ethyl Ketone in Polyisobutylene: Comparison of Gravimetric and Spectroscopic Techniques", *J. Polym. Sci.: Polym. Phys. Ed.*, 35, 1261-1267 (1997).

S. U. Hong, T. A. Barbari, and J. M. Sloan, "Multicomponent Diffusion of Methyl Ethyl Ketone and Toluene in Polyisobutylene from Vapor Sorption FTIR-ATR Spectroscopy", *J. Polym. Sci.: Polym. Phys. Ed.*, 36, 337-344 (1998).

S. U. Hong and T. A. Barbari, "Single and Multicomponent Diffusion at Infinite Dilution in Polyisobutylene", *Polym. Int.*, 48, 901-908 (1999).

Y. A. Elabd, J. M. Sloan, and T. A. Barbari, "Diffusion of Acetonitrile in Conformational Isomers of H₁₂MDI Polyurethane", *Polymer*, 41, 2203-2212 (2000).

In Preparation and Based on Work Supported by this Grant:

S. S. Kasargod, T. A. Barbari, and J. J. Plunkett, "Diffusion of Self-Associating Small Molecules in a Polymer above its Glass Transition"

S. S. Kasargod and T. A. Barbari, "Spectroscopic Evidence of Anomalous Methanol Transport in Polycarbonate"

Scientific Personnel Supported on this Grant

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DRUG QUALITY IMPROVEMENT

Inventions

None

Scientific Accomplishments

Transport models were developed for diffusion with self-association or intersolute solvation through a membrane. Defining permeation breakthrough as the time at which a specified amount of penetrant has accumulated downstream of the membrane, numerical solutions for the transient portion of the cumulative flux expression were used to determine the effect of association or solvation on the breakthrough time. At low fractions of unassociated or unsolvated penetrant at the upstream surface, the breakthrough time increased with decreasing mobility of the associated or solvated species. However, the effect of finite kinetics resulted in breakthrough times that were either greater or less than those at local equilibrium, depending on the mobility of the associated or solvated species. These results can be explained in terms of local sources and sinks of penetrant. For materials of equivalent penetrant solubilities, those in which the equilibrium strongly favors the formation of immobile clusters or complexes will have measurably longer breakthrough times.

The transport model developed to account for penetrant self-association is being applied to methanol and ethanol transport in crosslinked polybutadiene, measured from the liquid phase using FTIR-ATR spectroscopy. In applying the model to the data, the assumption of local equilibrium, often made in modeling diffusion with association, is being tested. The self-association model was modified for methanol transport in glassy polycarbonate. An overshoot was observed for unassociated methanol with the spectroscopic technique, while typical Fickian behavior was observed for the self-associated methanol. The observed behaviors can only be captured with a Fickian transport model when local equilibrium is relaxed in the bulk and at the external boundary. Two manuscripts are currently in preparation describing these results.

FTIR-ATR spectroscopy was combined with a conventional gravimetric sorption balance to compare diffusion coefficients obtained from the two techniques from the vapor phase. Mutual diffusion coefficients for methyl ethyl ketone (MEK) in polyisobutylene (PIB) were measured with both methods at various solvent activities and temperatures in the range 40-60°C. The concentrations in the polymer were determined from the sorption balance. The diffusion coefficients from the two techniques agreed very well. In addition, the diffusion coefficients could be correlated with the Vrentas and Duda free volume model.

Diffusion coefficients of toluene/methyl ethyl ketone (MEK) mixtures in polyisobutylene were measured at 50°C using vapor sorption FTIR-ATR spectroscopy. For three mixture compositions, the diffusion coefficients were determined using a diffusion framework for a ternary system. The "crossterm" diffusion coefficient for MEK was found to be very small under the experimental conditions studied, while that for toluene was found to increase with increasing MEK concentration. On the basis of this finding, a binary diffusion model was used

to determine diffusion coefficients for MEK over a wider range of mixture compositions and the results compared well with those determined from pure MEK transport data. Relative transport rates during integral sorption experiments with mixtures were used to explain the results.

The diffusion coefficient of the slower penetrant (toluene) is affected by the concentration gradients of both penetrants, while that of the faster penetrant (MEK) may be only affected by its own concentration gradient for certain mixture compositions. Physically, the faster penetrant in an integral sorption experiment may be influenced primarily by the free volume of the polymer while the slower penetrant appears to be influenced by the additional free volume introduced by the faster penetrant. A similar conclusion would be drawn for the transient portion of a membrane permeation experiment. Therefore, a barrier membrane designed to prevent the transport of a faster-diffusing penetrant can be characterized on the basis of a binary diffusion model applied to mixture data under certain conditions. Further studies are needed to elucidate the conditions over which this result can be applied generally.

Diffusion coefficients of acetone, benzene, chloroform, cyclohexane and methyl ethyl ketone (MEK) in polyisobutylene (PIB) were measured at temperatures in the range 40 - 70°C using capillary column inverse gas chromatography (CCIGC). The measured diffusion coefficients for the PIB/MEK system, considered to be at infinite dilution of the solvent, agreed very well with those determined previously from gravimetric and FTIR-ATR spectroscopic techniques when extrapolated to the limit of zero MEK concentration. The Vrentas - Duda free-volume theory for diffusion was used to correlate the diffusion coefficients at infinite dilution as a function of temperature, and the effect of solvent size on the diffusion process in PIB was studied. In addition, diffusion coefficients of MEK/toluene and MEK/ethanol mixtures in PIB were measured at 50°C. The CCIGC model for binary systems was used to determine diffusion coefficients for each solvent individually over a wide range of mixture compositions. The resulting values were identical to those determined from pure component data, confirming the hypothesis that the diffusion coefficient at infinite dilution is independent of a second infinitely-dilute component, with or without solvation between mixture components.

The diffusion of acetonitrile in conformational isomers of the aliphatic polyurethane, H₁₂MDI (4,4'-dicyclohexylmethane diisocyanate) / BD (1,4-butanediol) / PTMO (poly (tetramethylene oxide)), was investigated at a fixed hard segment content of 29.9 wt%. The effective diffusion coefficient, measured experimentally using FTIR-ATR spectroscopy, decreased as the trans-trans percentage in the hard segment increased. The spectra for the polyurethanes revealed higher fractions of hydrogen-bound C=O (carbonyl) groups at higher trans-trans percentages, which was consistent with higher values of hard segment T_g. During acetonitrile diffusion experiments, a shift from hydrogen-bound to free carbonyl groups in the hard segment domains occurred and hydrogen-bound C≡N and NH peaks appeared suggesting that acetonitrile is solvating to the hard segments in the polymer. Based on these findings, the trend observed for the effective diffusion coefficient was attributed to tortuosity and penetrant solvation in the polyurethane. Future work will couple these results with those from small-angle x-ray scattering (SAXS) on the same materials to separate morphology effects from solvation effects.

Technology Transfer

Interactions with ARL scientists occurred during the entire project period. The primary interaction was with Dr. James Sloan, a visiting scientist from Aberdeen Proving Ground, Maryland. The Materials Center of Excellence at Johns Hopkins University, an ARL-funded center, supported a related project during this time titled "Characterization of Polymeric Barrier Materials Using Diffusion Probe Spectroscopy." The focus of the ARL project was on the transport characterization of phase segregated polymers such as polyurethanes and block copolymers.